# Adaptive Measurement Control for Calorimetric Assay

Jeffrey G. Glosup
Michael C. Axelrod

October 1994

Lawrence
Livermore
National
Laboratory

# ADAPTIVE MEASUREMENT CONTROL FOR CALORIMETRIC ASSAY

Jeffrey G. Glosup, Lawrence Livermore National Laboratory, P. O. Box 808,
Mail Stop L-195, Livermore, CA 94551, USA, 510/423-0657 and
Michael C. Axelrod,  Lawrence Livermore National Laboratory, P. O. Box 808, Mail Stop
L-200, Livermore, CA 94551, USA, 510/422-0929

**Abstract:** The performance of a calorimeter is usually evaluated by constructing a Shewhart control chart of its measurement errors for a collection of reference standards. However, Shewhart control charts were developed in a manufacturing setting where a observations occur in batches. Additionally, the Shewhart control chart expects the variance of the charted variable to be known or at least well estimated from previous experimentation. For calorimetric assay, observations are collected singly in a time sequence with a (possibly) changing mean, and extensive experimentation to calculate the variance of the measurement errors is seldom feasible. These facts pose problems in constructing a control chart.  In this paper, we propose using the mean squared successive difference to estimate the variance of measurement errors based solely on prior observations. This procedure reduces or eliminates estimation bias due to a changing mean. However, the use of this estimator requires an adjustment to the definition of the alarm and warning limits for the Shewhart control chart. We propose adjusted limits based on an approximate Student's *t*-distribution for the measurement errors and discuss the limitations of this approximation. Suggestions for the practical implementation of this method are provided also.

## 1. Introduction

The operational procedure for a calorimeter should contain some procedures to ensure that the measurement process remains in statistical control. Within the U.S. Department of Energy (DOE) complex, it is required that at least every fifth calorimetric measurement be made on an approved standard and the measurement errors of these standards are used to verify that the instrument is in statistical control. The accepted methodology for demonstrating statistical control is the classic Shewhart control chart, which is also referred to in the statistical literature as the Xbar chart.

A brief description and history of the development of the Shewhart chart is provided in Section 2 below. This description stresses the importance of grouped data in the

development of the Shewhart chart. This section also reviews and critiques existing recommended methods for creating Shewhart charts from observations that occur singly. Section 3 proposes an improved method for estimating the variability of observations that occur singly. Section 4 describes the procedures for constructing a modified control chart using this new estimator and offers some suggestions on its uses and limitations. Section 5 demonstrates the use of the modified control charting procedure with an example.

## 2. A Review of the Development and Use of Shewhart Control Charts

The idea of using "control charts" to monitor the precision and accuracy of manufacturing processes was introduced by Walter A. Shewhart, a researcher at Bell Telephone Laboratories, in the early 1930's. Much of the motivation and theory behind the production of control charts were set out in two books by Shewhart [Shewhart (1931) and Shewhart (1986),which is a reprint of a set of notes from lectures delivered to the Graduate School of the U. S. Department of Agriculture in 1939]. More modern accounts of the methods of statistical process control, especially the production of Shewhart charts, are discussed by John (1990), Wetherill (1991), and Bissell (1994).

In general, the methods developed by Shewhart in the 1930's, assume that the process to be monitored is a manufacturing process and that this process produces lots or batches of the product (e.g. widgets). The quality of a batch of widgets is measured by some attribute denoted by $x$. The quality of the batches, as measured by $x$, is said to be in statistical control if the mean and variance of $x$ are constant. However, the object we refer to as the Shewhart chart is designed only to detect changes in the mean of $x$. Throughout the remainder of this paper, we assume that statistical control only refers to a constant mean; details of procedures for detecting nonconstant variance are available in Wetherill (1991) and Bissell (1994).

The quality of the batches over time is monitored by taking a sample of size $k$ from each of $n$ lots produced over the time interval of interest and calculating the sample mean $\bar{x}_i$ and sample variance $s_i^2$ for lots $i = 1,\ldots,n$. Then the sample means $\bar{x}_i$ are plotted against lot number $i$ for $i = 1,\ldots,n$ with the sample mean as the ordinate and the lot number as the abscissa. This plot, which is referred to as the Shewhart chart, is used to make statistical inferences about the control of the quality attribute $x$. In order to simplify the statistical inference procedures, two assumptions about the sample means $\bar{x}_i$ are made: the

sample means are normally distributed, and they are statistically independent (i.e. the lots are independent). Additionally it is assumed that the quality attribute $x$ has constant mean value $\mu$ and constant variance $\sigma^2$. Often $\mu$ is referred to as the target value of the process.

The statistical control of the process is monitored by adding three horizontal lines to the Shewhart chart plot. The first line added is a centerline which is located at the target value $\mu$ if it is known or at the grand mean

$$\bar{\bar{x}} = \frac{1}{n}\sum_{i=1}^{n}\bar{x}_i \tag{1}$$

of the sample means if $\mu$ is not known. The other two lines are the control or alarm limits. If the variance $\sigma^2$ of the quality attribute $x$ is known, these are located at the centerline $\pm$ $3.09\,\sigma/\sqrt{k}$. If the variance $\sigma^2$ is not known, the alarm limits are located at the centerline $\pm$ $3.09\,s_{TOT}/\sqrt{k}$ where $s_{TOT}^2$ is the total estimated variance of the process. In both cases, the constant 3.09 is the 99.9th percentile of a standard normal distribution although its value is often truncated to 3.00. The process is said to be in statistical control (i.e. it has a constant mean for the quality attribute $x$) if all of the plotted values of $\bar{x}_i$ fall between the upper and lower alarm limits. If any one of the $\bar{x}_i$ falls outside the alarm limits, the process is said to be out of control, and the cause of the out of control signal needs to be identified and corrected. More recent control charting theory adds warning lines to the Shewhart chart as well. The warning lines are located at the centerline $\pm\,1.96\,\sigma/\sqrt{k}$ (centerline $\pm$ $1.96\,s_{TOT}/\sqrt{k}$ if $\sigma^2$ is not known). The constant 1.96 is the 97.5th percentile of the normal distribution, and it is frequently rounded to 2.00. If any two consecutive sample means fall outside the warning limits but not outside the alarm limits, the process is also said to be out of control, see John (1990) or Bissell (1994).

In the (usual) case where the variance $\sigma^2$ is not known, the total estimated variance $s_{TOT}^2$ can be calculated from the sample means $\bar{x}_i$ and sample variances $s_i^2$ for $i = 1,\ldots,n$. If the variation of the quality attribute $x$ of the widgets is assumed to occur completely within the lots, with negligible variation in mean between the lots, and if the sample size $k$ is constant for all lots, the total estimated variance is

$$s_{TOT}^2 = \frac{\sum_{i=1}^{n}s_i^2}{n}. \tag{2}$$

If some variation in mean value between lots is expected, a more complicated formula for the total estimated variance can be used; see Chapter 3 of Wetherill (1991). However, in all cases, the grouping of the individual measurements $x$ into batches is an essential ingredient allowing calculation of the total estimated variance and the production of the control chart.

If the quality attribute data $x$ does not naturally occur in batches, the preferred method of charting the data is to create artificial batches, which are referred to as rational subgroups. A rational subgroup is a collection of observations apparently having the same mean value although the mean value may vary between subgroups. If such a grouping is feasible, the rational subgroups can be treated as batches and the methods discussed above are directly applicable. However, there are situations where reasonable rational subgroups cannot be formed. The control charting of measurement errors in calorimetric assay is one of those situations since each measurement takes a significant fraction of a day to complete, and the environmental factors which may affect the measurement process change on roughly the same time scale.

Some procedures have been developed for producing Shewhart control charts for observations that occur singly over time and cannot be formed into rational subgroups (these are referred to as one-at-a-time data). Clearly, the one-at-a-time data can be plotted against observation number (or time of observation if desired) and a grand mean $(\bar{x})$ can be used to estimate the centerline for the control chart if the target value $\mu$ is unknown. However, in order to obtain control limits, the variability of the process will have to be estimated (assuming $\sigma^2$ is not known), and two assumptions will have to be made: the quality attribute $x$ is normally distributed and the any two observations of $x$ are statistically independent. Experience indicates that for calorimetric data, these last two assumptions are often reasonable, but need to be verified on a case by case basis.

The main problem that arises in producing the control chart is that estimating the variability of the process is now more difficult. The naive procedure would be to use the standard estimator of the variance

$$s^2 = \frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1} \tag{3}$$

where $n$ is the number of observations available. However, this estimator is biased if the observations $x$ are serially correlated or if the true mean of the variable $x$ is not a constant. Thus in situations where the mean of the quality attribute varies over time; e.g. as a systematic function or random walk, this estimator will produce an estimated variance that is biased (usually too large) and this will lead to false out of control signals occurring with much different probability than expected .

As an alternative to the usual variance estimate, modern work on control charts suggests using an ad-hoc method for estimating the process variation. One method suggested by Wetherill (1991) is the method of moving ranges. This method calculates the ranges of groups of observations of size $k$ for $k = 2, 3,…$ and estimates the variance as a scale constant times the mean of the ranges for a particular value of $k$ (where the mean is taken relative to the number of ranges, not the number of observations). The appropriate scale factors are provided in Chapter 6 of Wetherill (1991). The best $k$ for defining the estimator is chosen subjectively by plotting the variance estimates as a function of $k$. It is unclear what the bias and variance of this estimator are because of its subjective nature. Wetherill (1991) also indicates it is not an appropriate estimator if the mean of the process contains a linear trend. Thus it is obvious that a new, more robust method for calculating the variation of the process is needed for one-at-a-time data.

## 3. An Improved Method for Estimating the Variability of a Process

As seen in the previous section, little work has been done within the field of control charting towards fully adapting the methodology to one-at-a-time data. The main problem involves estimating the variance of the quality attribute $x$ which is to be plotted in the control chart. The usual estimator of standard deviation is very sensitive to a randomly or systematically drifting mean and so leads to an estimate that is biased. The ad-hoc method for estimating the process variance mentioned above is very subjective and it is unclear how it reacts to violations in the assumptions of constant mean of the process. However, a method for objectively estimating the variance of the quality attribute $x$ using the mean squared successive differences (MSSD) of the observations has been proposed by several people [Scholz (1994) and Marquardt (1993)] although these proposals have not yet entered the mainstream of statistical literature. The goal of this section is to describe the

properties of the MSSD as an estimator of the process variance and describe how the Shewhart control charting procedure can be modified to use this new estimator.

The MSSD was first suggested as a variance estimator by researchers studying artillery ballistics, see von Neumann (1941). It was developed to reduce the bias of the variance estimate caused by a nonconstant mean value of the variable $x$. The MSSD estimator of the variance is defined as

$$s^2_{MSSD} = \frac{\sum_{i=1}^{n-1}(x_{i+1} - x_i)^2}{2(n-1)}. \tag{4}$$

As can be seen from the definition, this estimator does not measure the distance of each point from the sample mean but only the distance between consecutive points. This allows the MSSD to estimate the variance of the process with less bias than the standard estimator in cases where the mean is randomly or systematically (not necessarily linearly) varying. In fact, this estimator forms a key piece of the von Neumann ratio test for independence (versus an alternative of serial correlation) of normally distributed observations, see Chapter 6 of Brownlee (1965) , Chapter 11 of Lindgren (1976), or Chapter 3 of Madansky (1988).

Assuming that consecutive values of the variable $x$ are independent, the MSSD estimator of the variance is

$$E\left[s^2_{MSSD}\right] = \sigma^2 \tag{5}$$

which means it is an unbiased estimator of the variance; see Brownlee (1965) or von Neumann (1941). The variance of the MSSD estimator of the variance is

$$Var\left[s^2_{MSSD}\right] = \frac{3n-4}{(n-1)^2}\sigma^4, \tag{6}$$

see von Neumann (1941). For the case where the observations $x$ are independent with constant mean and variance, the usual estimator of the variance is also unbiased, i.e. $E\left[s^2\right] = \sigma^2$, and its variance is

$$\mathrm{V}ar\left[s^2\right] = \frac{2}{(n-1)}\sigma^4. \tag{7}$$

Thus the efficiency[1] of $s^2_{MSSD}$ relative to $s^2$ is

$$\frac{2(n-1)}{3n-4} = \frac{2}{3}\left(1 + \frac{1}{3n-4}\right) \tag{8}$$

indicating that as $n$ gets very large, the variance of the usual estimator $s^2$ is 2/3 as large as the variance of the MSSD estimator; see von Neumann (1941). However, the efficiency in equation (8) is based on the assumptions that the observations are independent with constant mean and variance. In cases where the mean is not a constant, the bias of the usual estimator is larger than the bias of the MSSD estimator of variance. and the relative efficiency will be larger than 2/3 and can even become larger than 1, indicating that the MSSD estimator is a better estimator than the usual variance estimator $s^2$.

For the case where the observations $x$ are normally distributed with constant mean value $\mu$ and constant variance $\sigma^2$,the probability distribution of the variance estimator $s^2$ from equation (3) is well known to be proportional to the $\chi^2_{n-1}$ distribution (where the subscript $n$-1 is the degrees of freedom of the distribution); see for example Chapter 8 of Brownlee (1965). However, the probability distribution of the of the MSSD estimator $s^2_{MSSD}$ is not a simple distribution. The distribution function for the case where the observations $x$ are normally distributed with constant mean value $\mu$ and constant variance $\sigma^2$ is shown by von Neumann (1941) to be proportional to a Bessel function of order zero. However, since the estimator can be expressed as a quadratic form [see von Neumann (1941)], it was suggested by Scholz (1994) that an approximation due to Satterthwaite (1946) could be used for the sampling distribution of $s^2_{MSSD}$. This approximation assumes that the distribution of the estimator is proportional to a $\chi^2_d$ distribution where the degrees of freedom $d$ are chosen to make this approximate distribution as similar as possible to the true unknown distribution. For the $\chi^2_d$ distribution this consists of choosing $d$ so that the variance of the $\chi^2_d$ distribution, which is 2d, is equal to the variance of the ratio $ds^2_{MSSD}/\sigma^2$, which can be calculated using equation (6) above.

---

[1]Efficiency and relative efficiency are concepts that were introduced by R. A. Fisher in the 1920's; see Fisher (1921) for the original work or Kendall (1979) for a clear definition and discussion of the concepts.

Solving this equation, the appropriate degrees of freedom for the approximate distribution is

$$d = \frac{2(n-1)^2}{3n-4}.$$  (9)

Clearly, the degrees of freedom are less than $n$-1, the degrees of freedom of the usual variance estimator for $n$ observations. Figure 1 shows a plot of the value of $d$ as a function of $n$. Note that the relationship is nearly linear and can be accurately approximated by $d = 2(n-1)/3$.

**Figure 1**
**Degrees of Freedom as a Function of Sample Size**
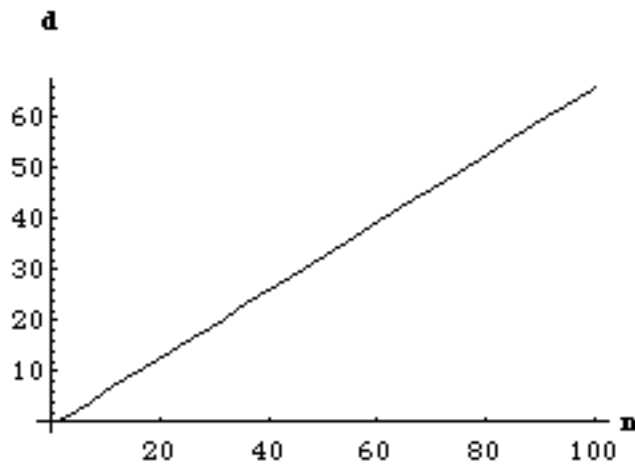


## 4. Constructing the Modified Control Chart

In order to construct the classical Shewhart control chart described in Section 2 for the case where the variance $\sigma^2$ is known, the alarm/warning limits were calculated using the pivotal quantity[2]

---

[2]For a definition of the pivotal quantity and a discussion of its use in forming confidence intervals and constructing hypothesis tests, see Lindgren (1976). For the connection between control charts, confidence intervals and hypothesis tests, see John (1990).

$$Z = \frac{\bar{x}_i - \text{centerline}}{\sqrt{\sigma^2/k}}. \qquad (10)$$

This pivotal quantity is normally distributed since the Central Limit Theorem provides that $\bar{x}_i$ will tend to be normally distributed and the denominator and the centerline are constants. In the case where the variance $\sigma^2$ is not known, it is replaced by its estimate $s^2_{TOT}$ . To be exact, the pivotal with the true variance replaced by its estimate should have Student's $t$-distribution with $n(k$-1) degrees of freedom; see, for example, Chapter 9 of Brownlee (1965). However, in most cases of classically constructed Shewhart control charts, the product $n(k$-1)is so large that the $t$-distribution is essentially equivalent to the normal distribution and there is little error in assuming the pivotal quantity is again normally distributed.

The control chart to be produced with the MSSD estimate of the process variance should have alarm/warning limits based on pivotal quantity

$$t = \frac{x - \text{centerline}}{\sqrt{s^2_{MSSD}}}. \qquad (11)$$

If $x$ is normally distributed with mean = centerline, and the numerator and denominator of equation (11) are independent, this pivotal quantity will approximately have Student's t-distribution since we know the term $s^2_{MSSD}$ approximately proportional to a $\chi^2_d$ distribution. As mentioned previously, the quality attribute $x$ for a calorimetric measurement process, which is the measurement error, is frequently normally distributed, and because an individual observations $x$ forms only a small part of the denominator term, an assumption of independence is likely to be approximately correct. Some simulation experiments on the correctness of the $t$-distribution for the pivotal quantity in equation (11) as a function of $n$ are discussed further below in this section.

The alarm/warning limits for the modified chart are produced by specifying a desired false detection rate for the alarm/warning limit; let $\alpha$ denote the desired probability of a false detection of alarm/warning. This specification is used together with the appropriate $t$-distribution to find a critical-value $t_d(\alpha)$ for the alarm/warning limit so that

$$\Pr[t > t_d(\alpha)] = \frac{\alpha}{2}. \qquad (12)$$

For the alarm limit, the usual value of $\alpha$ is 0.002 and for the warning limit, the usual value of $\alpha$ is 0.05. Inverting the pivotal quantity in equation (11) and using the symmetry of the t-distribution, the alarm/warning limit is placed at $x = \text{centerline} \pm t_d(\alpha)\, s_{MSSD}$.

   To actually construct the modified control chart, a collection of approximately 10 observations needs to be obtained in order to start the variance estimator. Then as each additional observation is obtained, it should be charted against its observation number (or the time of observation). The centerline is added at the known (or estimated) target value and the appropriate alarm/warning limits for each observation are added at the centerline $\pm$ $t_d(\alpha)\, s_{MSSD}$ where $s_{MSSD}$ is calculated from all observations up to and including the plotted point. As each new observation is added, the total number of observations available increases by one and so the degrees of freedom $d$ increase by approximately 2/3. Thus, this control chart is adaptive in two senses: it adjusts the control limits to be tighter as more information is added to the calculation of the variation of the process, and since the variance of the process is updated with each added observation, it fluctuates, either up or down, with the natural process variation. That is, if the process variation naturally settles down over time, the estimated process variation will decrease and the alarm/warning limits will slowly shrink towards the centerline over time.

   A simulation study was performed to arrive at the approximate number of observations needed to start the process variance estimator. The simulation produced 1000 sets of $n$ observations from a normal random variable generator with mean = 0 and variance = 25. For each of these 1000 data sets, the pivotal quantity in equation (11) was calculated using the last observation in the data set in the numerator and the MSSD variance estimate in the denominator. Then the assumption that these pivotal quantities were $t$-distributed with $d$ degrees of freedom was checked using a quantile-quantile plot, see Chambers (1983) for details. This simulation study was repeated for 3 values of $n$; $n = 7$, 11, and 21. The resulting quantile-quantile plots are shown in Figures 2,3, and 4 respectively. The 1000 points plotted in each graph should follow a straight line if the assumed $t$-distribution is correct. Curvature away from a theoretical straight line indicates a departure from the assumed $t$-distribution. Clearly Figure 2 indicates that the assumed $t$-distribution is not correct for n = 7. However, for n = 11 and 21 the assumed $t$-distribution seems adequate. Thus the alarm/warning limits produced with 10 preliminary

observations, plus one additional observation, will be accurate. However, it would not be prudent to use fewer than 10 preliminary observations to start the control chart.

## 5. A Demonstration of the Modified Control Chart

The modified control charting procedure presented in the last section is demonstrated here by an example. The data used are the measurement errors from a heat-flow type calorimeter operated by Lawrence Livermore National Laboratory. The quality attribute being monitored is the relative measurement error

$$x = \frac{meas - std}{std} \tag{13}$$

where *meas* is the measured power of a standard in Watts and *std* is the calculated decayed power of the standard in Watts. The data used to produce the control chart, including the 10 preliminary points, are contained below in Table 1. Table 2 shows how the improved variance estimator is calculated. Column 2 of Table 2 contains the measurement errors from Table 1. Column 3 contains the successive differences of the measurement errors, and column 4 contains the square root of the MSSD estimator of the variance. Note that the MSSD estimate is not shown for the first 10 points since its distribution cannot be approximated in these cases.

Figure 5 shows the modified Shewhart control chart for the relative measurement errors over the period from July 19 through October 17 of 1994. Note that the centerline of the chart is set at -0.0025, a target value determined by previous experimentation. Figure 5 clearly shows how the alarm/warning limits tend to shrink as more information becomes available. However, it also demonstrates how the variance estimator, and hence the alarm/warning limits, respond to a large observation by increasing the distance from the center line to the alarm/warning limits.

## 6. Acknowledgments

**Table 1**

**Heat Flow Calorimeter Data Example**

| Date | Nominal Power (Watts) | Measured Power (Watts) | Mound Standard Power (Watts) | Relative Error |
|---|---|---|---|---|
| 6/9/94 | 1.00 | 0.999118 | 0.997949 | 0.001171 |
| 6/14/94 | 2.00 | 1.742863 | 1.741307 | 0.000894 |
| 6/21/94 | 0.10 | 0.095427 | 0.094642 | 0.008294 |
| 6/23/94 | 0.25 | 0.214220 | 0.214459 | -0.001115 |
| 6/24/94 | 0.10 | 0.093889 | 0.094636 | -0.007892 |
| 7/2/94 | 1.00 | 1.001856 | 0.998169 | 0.003694 |
| 7/6/94 | 0.100 | 0.093890 | 0.094611 | -0.007631 |
| 7/7/94 | 2.000 | 1.744063 | 1.740446 | 0.002078 |
| 7/8/94 | 0.500 | 0.419021 | 0.418954 | 0.000159 |
| 7/12/94 | 0.250 | 0.214562 | 0.214372 | 0.000887 |
| 7/19/94 | 1.000 | 0.999974 | 0.998330 | 0.001646 |
| 7/27/94 | 0.100 | 0.095086 | 0.094569 | 0.005475 |
| 8/3/94 | 0.100 | 0.094915 | 0.094554 | 0.003813 |
| 8/13/94 | 0.250 | 0.213194 | 0.214224 | -0.004808 |
| 8/23/94 | 0.100 | 0.094573 | 0.094514 | 0.000628 |
| 8/30/94 | 0.250 | 0.214904 | 0.214146 | 0.003538 |
| 9/8/94 | 0.100 | 0.094744 | 0.094481 | 0.002782 |
| 9/16/94 | 0.100 | 0.095086 | 0.094465 | 0.006573 |
| 9/23/94 | 0.100 | 0.093719 | 0.094451 | -0.007751 |
| 9/30/94 | 0.250 | 0.213024 | 0.214004 | -0.004579 |
| 10/17/94 | 0.100 | 0.093719 | 0.094402 | -0.007239 |

**Table 2**

**Calculation of MSSD Estimator of Variance for**

**Heat Flow Calorimeter Data Example**

| Date | Relative Error | Successive Differences | MSSD Estimate of Standard Deviation |
|---|---|---|---|
| 6/9/94 | 0.001171 | | |
| 6/14/94 | 0.000894 | -0.000277 | |
| 6/21/94 | 0.008294 | 0.007400 | |
| 6/23/94 | -0.001115 | -0.009410 | |
| 6/24/94 | -0.007892 | -0.006777 | |
| 7/2/94 | 0.003694 | 0.011587 | |
| 7/6/94 | -0.007631 | -0.011325 | |
| 7/7/94 | 0.002078 | 0.009709 | |
| 7/8/94 | 0.000159 | -0.001919 | |
| 7/12/94 | 0.000887 | 0.000728 | |
| 7/19/94 | 0.001646 | 0.000759 | 0.00016973 |
| 7/27/94 | 0.005475 | 0.003828 | 0.00081615 |
| 8/3/94 | 0.003813 | -0.001662 | 0.00033916 |
| 8/13/94 | -0.004808 | -0.008621 | 0.00169063 |
| 8/23/94 | 0.000628 | 0.005436 | 0.00102731 |
| 8/30/94 | 0.003538 | 0.002910 | 0.00053124 |
| 9/8/94 | 0.002782 | -0.000756 | 0.00013367 |
| 9/16/94 | 0.006573 | 0.003791 | 0.00065019 |
| 9/23/94 | -0.007751 | -0.014325 | 0.00238746 |
| 9/30/94 | -0.004579 | 0.003172 | 0.00051459 |
| 10/17/94 | -0.007239 | -0.002660 | 0.00042051 |

## 7. References

Bissell, D. (1994). *Statistical Methods for SPC and TQM*. New York, Chapman and Hall.

Brownlee, K. A. (1965). *Statistical Theory and Methodology in Science and Engineering*. New York, John Wiley & Sons, Inc.

Chambers, J. M., Cleveland, W. S., Kleiner, B. and Tukey, P. A. (1983). *Graphical Methods for Data Analysis*. Pacific Grove, CA, Wadsworth and Brooks/Cole.

Fisher, R. A. (1921). "On the mathematical foundations of theoretical statistics." *Philosophical Transactions of the Royal Society of London, A* **222**: 309-368.

John, P. W. M. (1990). *Statistical Methods in Engineering and Quality Assurance*. New York, John Wiley and Sons.

Kendall, M. a. S., A. (1979). *The Advanced Theory of Statistics, 4th ed.* London, Charles Griffin & Co. Ltd.

Lindgren, B. W. (1976). *Statistical Theory, 3rd. ed.* New York, MacMillan Publishing Co., Inc.

Madansky, A. (1988). *Prescriptions for Working Statisticians*. New York, Springer-Verlag.

Marquardt, D. W. (1993). *Estimating the standard deviation for statistical process control*. 153rd. Annual Meeting of the American Statistical Association, San Francisco, CA,

Satterthwaite, F. E. (1946). "An approximate distribution of estimates of variance components." *Biometrics Bulletin* **2**: 110-114.

Scholz, F. (1994). *Small Sample Uni- and Multivariate Control Charts for Means*. 154th Annual Meeting of the American Statistical Society, Toronto, Canada,

Shewhart, W. A. (1931). *The Economic Control of Manufactured Product*. New York, Van Nostrand.

Shewhart, W. A. (1986). *Statistical Method from the Viewpoint of Quality Control*. New York, Dover Publication, Inc.

von Neumann, J., Kent, R. H., Bellinson, H. R., and Hart, B. I. (1941). "The mean squared successive difference." *Annals of Mathematical Statistics* **13**: 153-162.

Wetherill, G. B., and Brown, D. W. (1991). *Statistical Process Control: Theory and Practice*. London, Chapman & Hall.
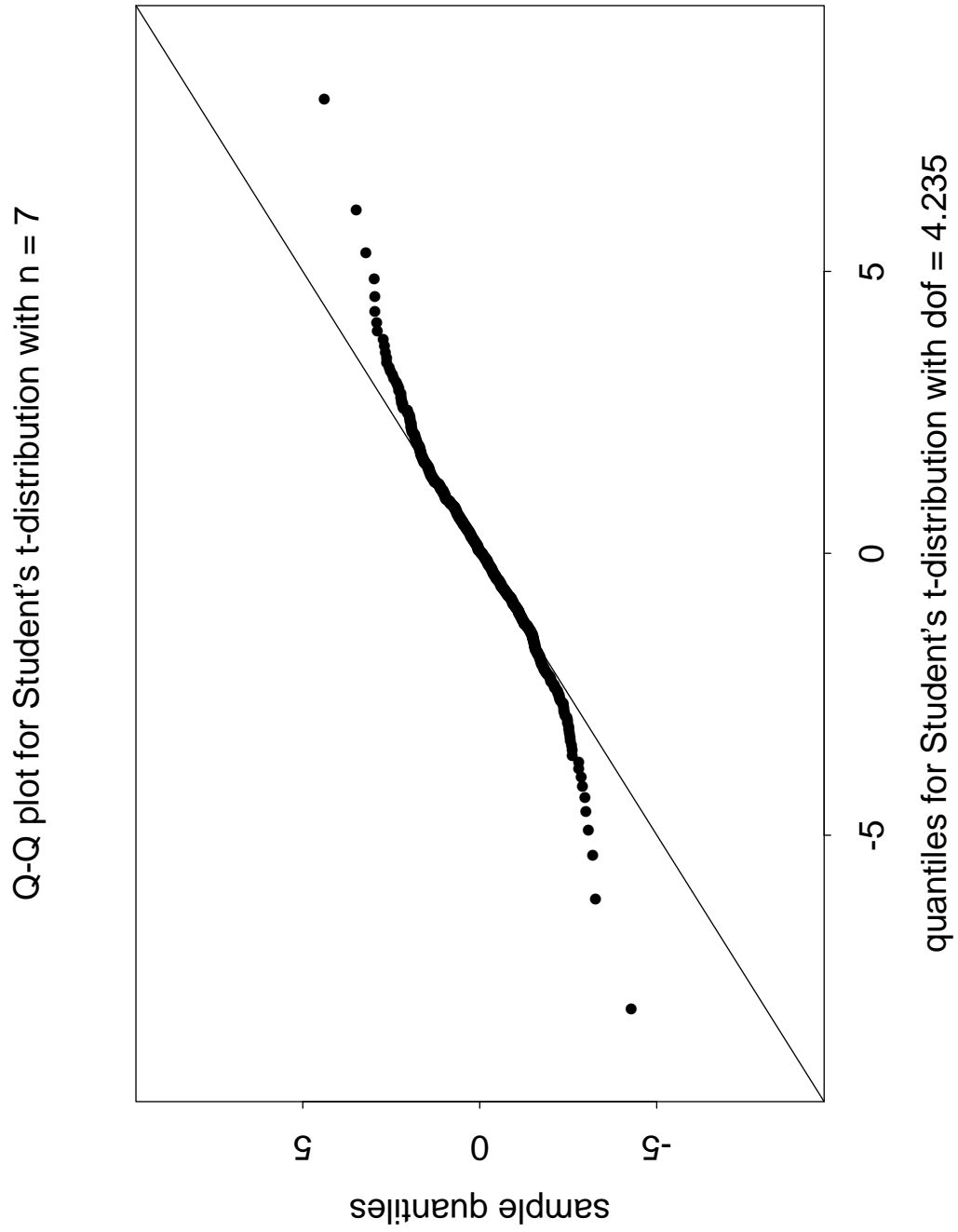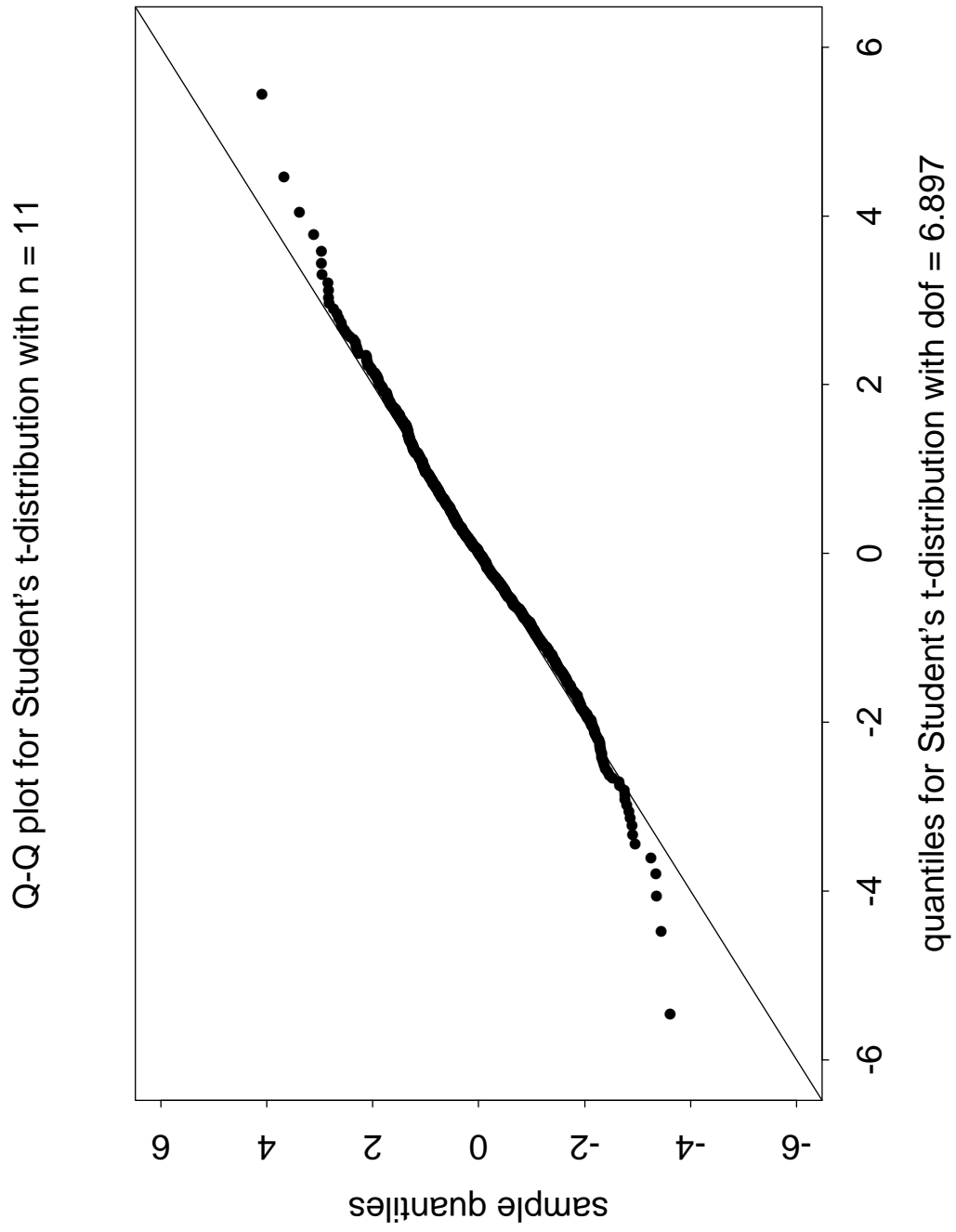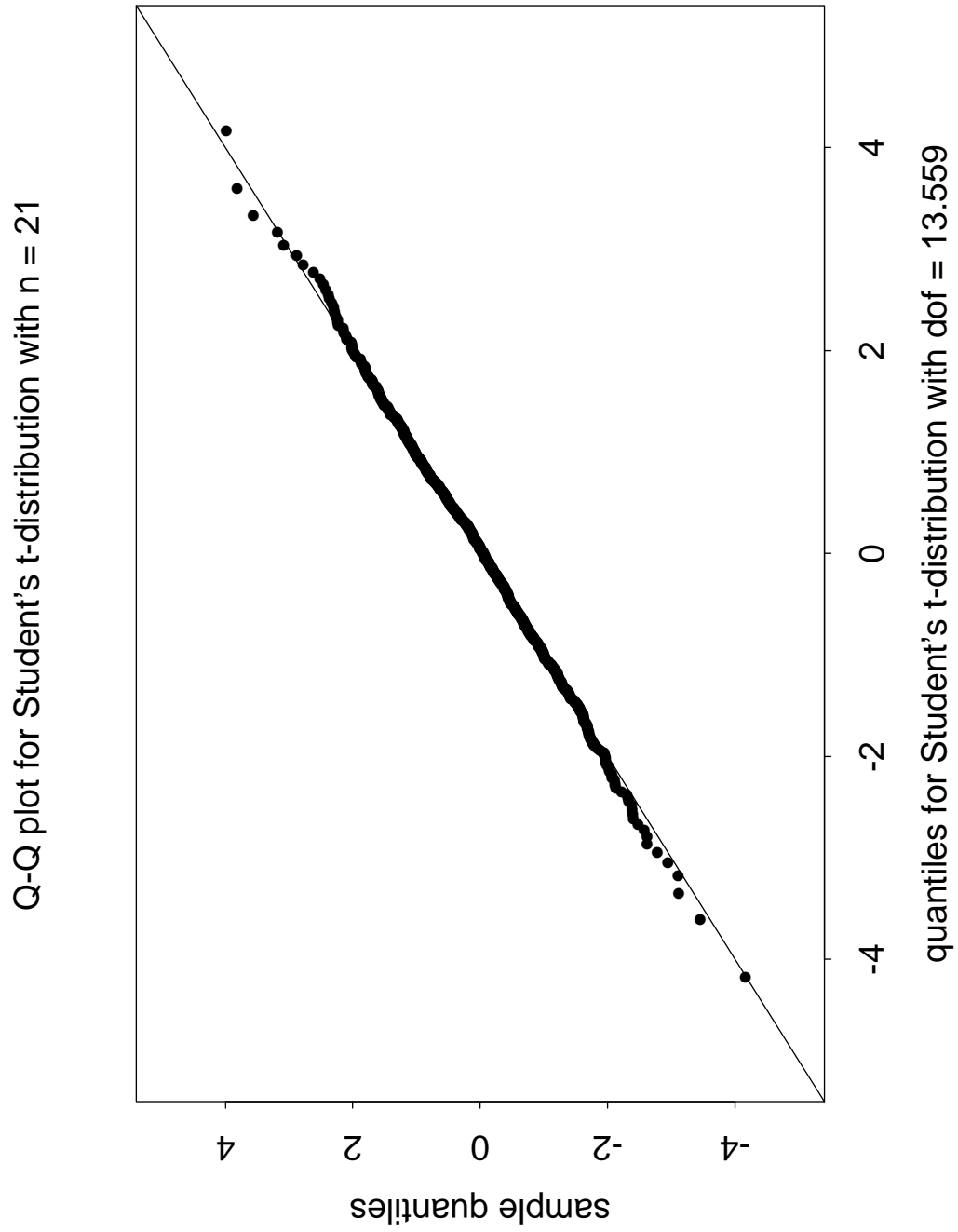
**Figure 2**



Q-Q plot for Student's t-distribution with n = 7

**Figure 3**



Q-Q plot for Student's t-distribution with n = 11

quantiles for Student's t-distribution with dof = 6.897

sample quantiles

**Figure 4**



Q-Q plot for Student's t-distribution with n = 21

**Figure 5**



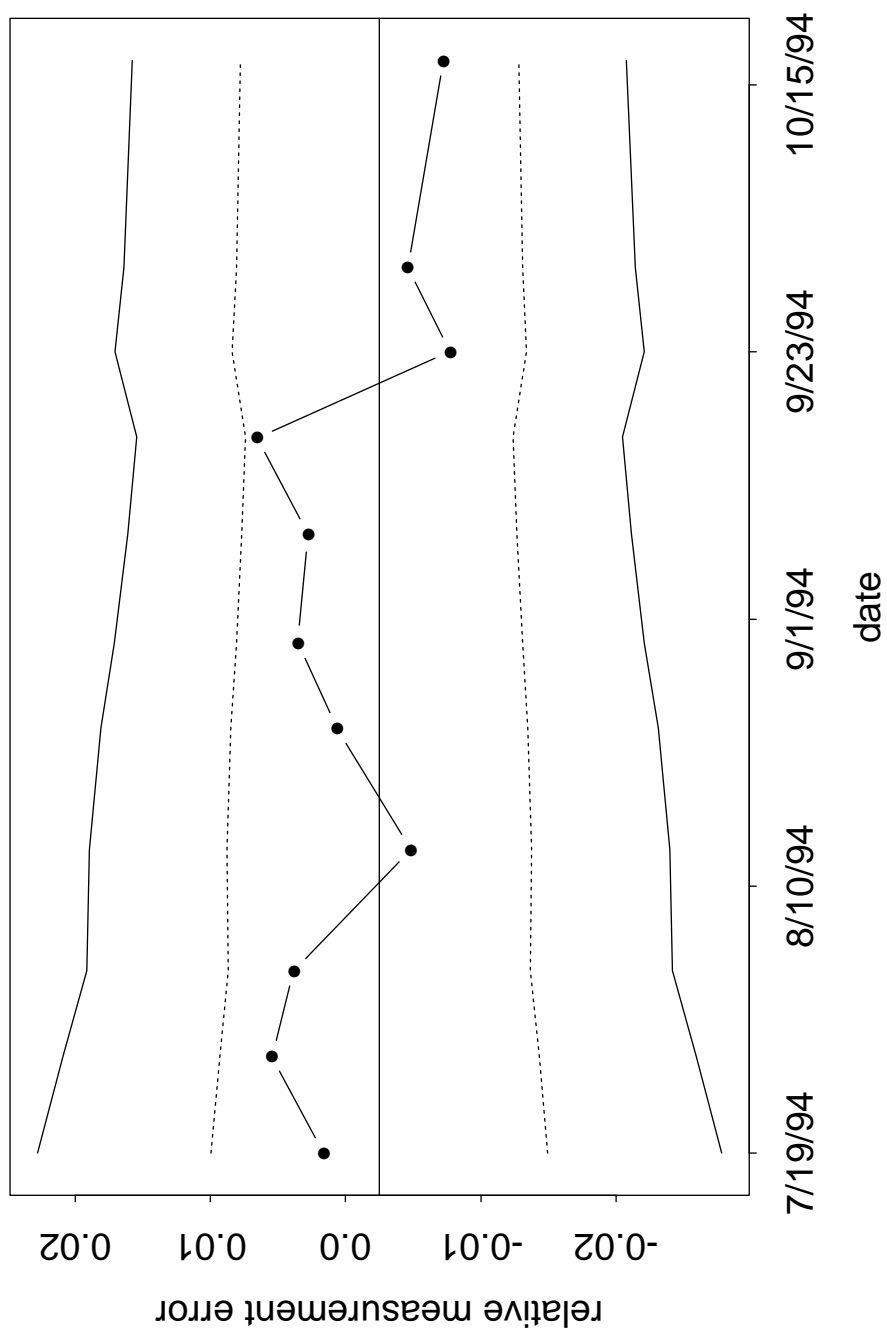Modified Shewhart control chart for a LLNL heat flow calorimeter